Modelling IR Spectra of Sulfonated Polyether Ether Ketone (SPEEK) Membranes for Fuel Cells

VAIVARS Guntars[1, a *], KRŪKLE-BĒRZIŅA Kristīne[2] and MARKUS Madara[2]

[1] Institute of Solid State Physics, University of Latvia, Kengaraga 8, Riga, Latvia, LV-1063

[2] Faculty of Chemistry, University of Latvia, Jelgavas 1, Riga, Latvia, LV-1004

[a]Guntars.Vaivars@cfi.lu.lv

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Abstract. SPEEK (sulfonated polyether ether ketone) membranes have been prepared and characterized. The SPEEK membrane geometry and theoretical vibration spectra calculated using density functional theory (DFT) as depending from membrane chain length and polymer cross-linking. Analyzed the limitations of the method by comparing theoretical and experimental IR spectra.

Introduction

The interest of the research, during the last 20 years, was addressed to the improvement of existing polymer electrolyte membranes for fuel cells and the development of new ones [1]. One of the most used and widely considered is sulfonated polyether ether ketone (SPEEK) because of its many advantages [2]. Proton exchange membrane (PEM) fuel cells have attracted increasing interest because of their efficiency, environmental compatibility, and higher power density [3].

The SPEEK as compared to the non-sulfonated polymer is highly hydrophilic and at high degree of sulfonation (DS) the solubility in water is observed [4] with progressively deteriorating mechanical properties [3]. The composite formation typically improves the mechanical strength of the membrane [3]. Most popular additives for composite formation are inorganic materials such as montmorillonite, SiO_2, TiO_2, ZrO_2 [5], or organic materials such as ionic liquids [6-8].

Cross-linking also improves the mechanical strength and there are different sulfonation routes producing variety of cross-linked products. The cross-linking also might decrease the water solubility [8-12]. Infrared spectroscopy is widely used to interpret the SPEEK structure [13] analyzing bond and stretching vibrations, providing information on intermolecular interactions [13,14]. However, the assignment for vibration bands is still controversial [11]. Recently, the theoretical calculations of the SPEEK membrane have been done and practical and theoretical spectra are reported by several groups already in order to assist the experiment [11,15-16].

Here, we will discuss the theoretical IS spectra of SPEEK depending on the monomer chain length and possible cross-linking.

EXPERIMENTAL AND RESULTS

SPEEK Synthesis. SPEEK was synthesized from polyether ether ketone (PEEK), obtained from Sigma Aldrich (number average molecular weight Mn ~10300, weight average molecular weight Mw ~20800) using sulfonation method with sulfuric acid (Sigma Aldrich, 95–97 %) as described before [8]. Sulfonation of PEEK carried out at 60 °C for 4 and 8h. SPEEK with DS= 0.30 and DS= 0.75 was obtained. SPEEK dissolved in N,N-dimethylformamide (DMF) and poured into Petri dishes and dried for 48 h at 80 °C. The SPEEK film removed from the Petri dish and used for carrying out further experiments.

For DS (in %) calculations following equation was used [8]:

$$DS = \frac{n(SO_3H)}{n(PEEK)} = \frac{M(PEEK)}{\left(\frac{m}{\Delta m}\right)M(SO_3H)},$$

where m is the mass of SPEEK, M(PEEK) is the molecular mass of the repeat unit n of PEEK (288.7 g/mol, Fig. 1), and M(SO_3H) that of sulfonic acid groups (81 g/mol).

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IR Spectra Analysis. ATR-FTIR spectra obtained with a Frontier FTIR spectrometer (Perkin-Elmer Inc., Norwalk, CT, USA) with a Universal ATR Sampling Accessory attachment. A background spectrum was recorded and subtracted from each recorded sample spectrum. Sample spectrum recorded by placing small piece of the membrane film in contact with the diamond ATR crystal. ATR-FTIR spectra recorded over the 4000-650 cm^{-1} range with 2 cm^{-1} resolution and built up over 16 scans per sample.

The geometry optimizations and vibration spectra calculations performed using density function theory (DFT), employing the B3LYP hybrid functional and 6-31G basis set. All calculations were performed using Gaussian program [17]. Gabedit [18] was used to visualize the structure and vibration spectra (Fig. 4 and Fig. 6).

The SPEEK structure geometry optimization and vibration calculations are difficult due to the large size and complicated nature of the system. Here, the simulations started from simple model (see Fig.2a) and carried on to the more complex including cross-linking (see Fig.2b and Fig.2c). The cross-linking included classical sulfur bridge (Fig.2b) and it was compared with hypothetical oxygen bridge (Fig.2c).

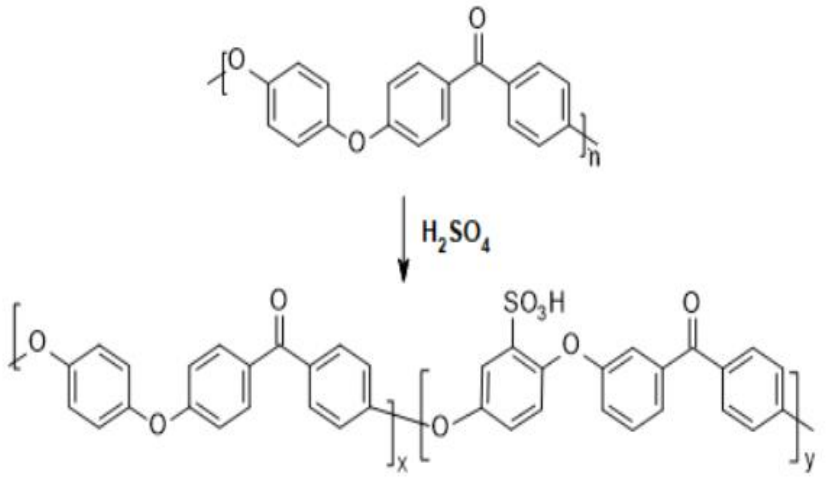

Fig. 1. Sulfonation procedure of PEEK

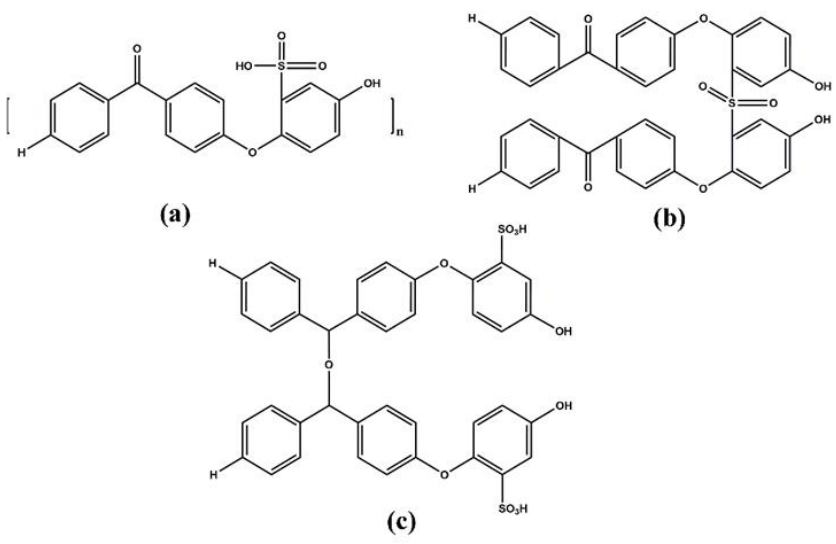

Fig. 2. Structure of investigated SPEEK structures: (a) – repeat unit n=1, 2, 4 and 6; (b) – cross-linked with sulphuric atom; (c) – cross-linked with oxygen atom

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The water interaction with sulfonic acid excluded from doing quantum chemical calculations. The theoretical calculated infrared spectra of the SPEEK depending from chain length (n=1, 2, 4 and 6) is shown in Fig. 3. Over-sulfonation leads to excessive swelling and membrane deterioration in water [8] . For applied purposes, the DS in the range from 0.7 to 0.8 are typically used. In this case, a simplified simulation model applied the DS equal to 1.

The optimized geometry of the SPEEK polymer chains (see Fig. 4) with different monomer length show reasonable changes going from a single monomer (n = 1) to a chain combined from few monomer units (n = 2 and n = 4). However, no visible changes observe for chains combined from 4 and more monomer units (Fig. 3, n = 4, n =6)).

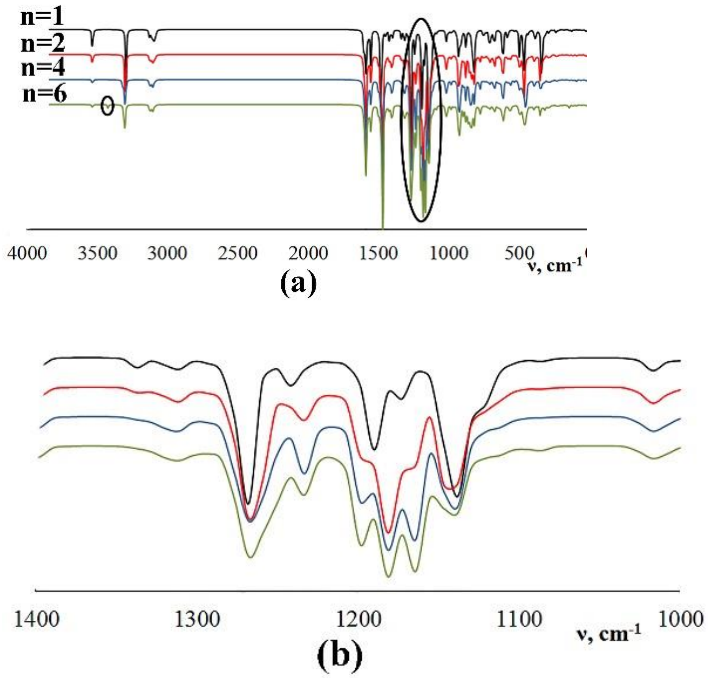

Fig. 3. The theoretical infrared spectra of the SPEEK depending from monomer chain length

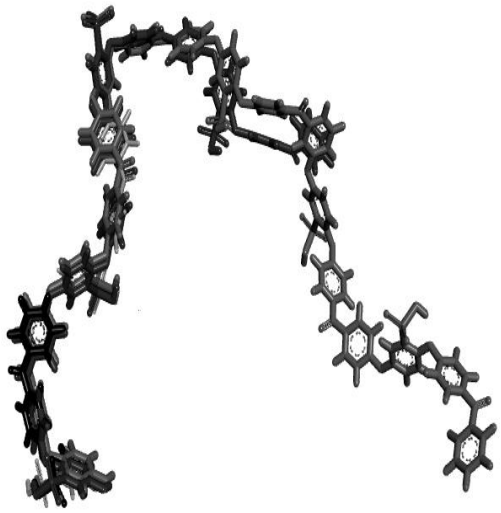

Fig. 4. The optimized geometry of the SPEEK depending from monomer chain length (n=1, 2, 4 and 6)

The SPEEK monomer can form chains, but also cross-linking with side chain monomers can take place. In the literature two suggestions are provided [8, 12] and it is shown in Fig. 1b and Fig. 1c. The cross-linking may take place between two sulphur atoms or/and two oxygen atoms. In case of cross-linking the theoretically calculated spectra show larger difference as compared to the previous ones (Fig. 5). If two sulphuric atoms are cross-linked the theoretical calculations shows that –OH groups at the end are forming hydrogen bonds with oxygen atoms from side monomer (see Fig. 6) therefore there is no atom vibration at 3300 cm^{-1} but it occurred at 3182 cm^{-1}. In addition, fewer vibrations observe on IS if sulphuric atoms are cross-linked. For two cross-linked oxygen atoms the sharp peak at 1588 cm^{-1} diminishes because less group vibrations on molecule occurred.

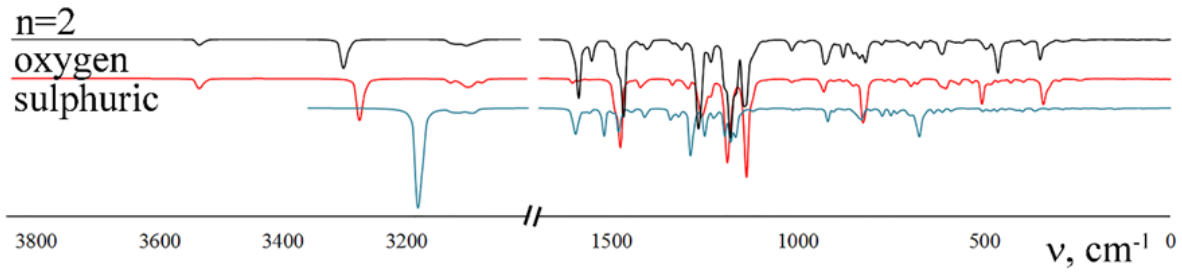

Fig. 5. The theoretical infrared spectra of the SPEEK in case of cross-linking with side monomer chain (main chain length is equal to 2)

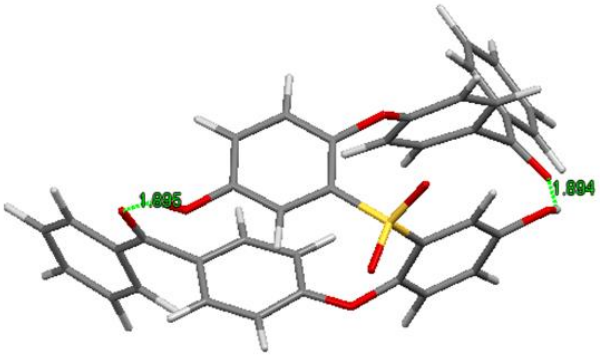

Fig. 6. The optimized geometry of the SPEEK cross-linked with sulphuric atom

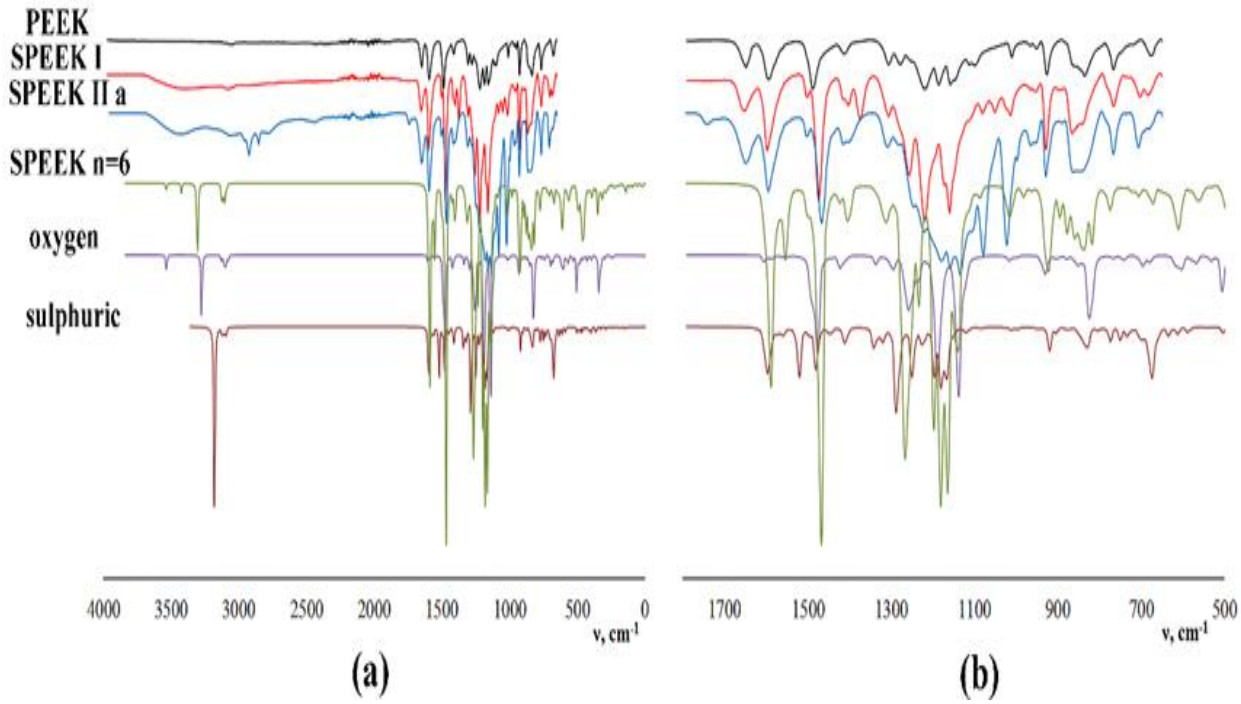

Fig. 7. The theoretical (SPEEK n=6, DS=1; cross-linked with oxygen and sulphuric) and experimental (PEEK; SPEEK I, DS= 0.30 and SPEEK II a, DS= 0.75) infrared spectra for SPEEK: (a) in a range 3600-600 cm^{-1}; (b) 1800-600 cm^{-1}

Experimental spectra (Fig. 7) show similar character to literature data [16]. A broad band in a 3600-3290 cm^{-1} range in experimental infrared spectra characterize increased hygroscopicity and water content for sulfonated PEEK. In this range also the –OH group stretching from sulfonic acid group occurs. At the same time, the theoretical spectra reveal sharp signals. The other broadband region at 1300-1100 cm^{-1} show peaks, which correspond to stretching and rocking vibrations typical for SPEEK. In the calculated infrared spectra, observe well-separated peaks in this region. In the calculation process the other possible interactions with side molecules and bond stretching is not included. The new peaks observed for sulfonated samples at 1024 and 1080 cm^{-1} correspond to symmetric and asymmetric stretching vibration of the sulfonic acid group in SPEEK. Both oxygen and sulphuric spectra calculated for two monomers and it does not take in account other possible interactions. However, they supported the idea that rather sulphuric atoms as oxygen are involved in SPEEK cross-linking.

Conclusions

Theoretical infrared spectra calculations are important for polymer membrane characterisation. Highly conductive and mechanically strong SPEEK polymer membrane preparation includes sulfonation and cross-linking, which results in variety of possible products depending on synthesis condition. Theoretical calculations confirm that the IR spectroscopy is useful to identify the cross-linking species. However, in many cases significant structural changes would not reflect in IR spectrum. The presence of monomer can identify, but longer chains will show no difference. The peak shift in a range 1100- 1200 cm^{-1} (Fig. 7) may indicate the presence of short chain length polymer. It is known that the variation of chain length will increase the ion conductivity of polymer. By comparing theoretical and experimental IR spectra, it is possible to identify the limitations of the method. Modern computing allows proceeding to more complex structures. Mechanical properties of SPEEK are limiting the practical applications and therefore new cross-linking procedures are welcomed. Theoretical calculations revealed that the oxygen bridging is theoretically possible. However, it should be confirmed experimentally. The work done and described in this paper is the first step and it will elaborate in further studies.

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